Acidification and recovery of aquatic ecosystems in south central Ontario, Canada: regional application of the MAGIC model

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Acidification and recovery of aquatic ecosystems in south central Ontario, Canada: regional application of the MAGIC model

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Abstract:

The dynamic model MAGIC was applied to 25 lakes in south-central Ontario, Canada using a regional modelling methodology. Soil and lake water chemistry for each lake catchment was simulated for the period 1850–2050. Sulphate (SO_4^{2-}) deposition forecasts were derived from recently proposed emission reductions, which correspond roughly to a 50% reduction in SO_4^{2-} deposition by 2010 from the 2000 baseline. Changes in SO_4^{2-} deposition had a significant impact on lake chemistry. Simulated lake water chemistry showed a recovery potential under the current deposition scenario; by 2050 concentration levels recovered to values predicted for the early 1900s. Moreover, simulated future lake water chemistry showed significant recovery compared to 1975 levels. However, although regional simulations predict that base cation losses have decreased in recent years, soils in the region will continue to acidify with Ca^{2+} losses dominating depletion of the exchangeable pool. Base cation losses from the exchangeable pool are currently buffering lakes against the impacts of acid deposition; ultimately base cation inputs into the lakes will decrease as exchangeable base cation pools become depleted. Further emission reductions are necessary to ensure continued recovery from acidification.

Keywords: regional dynamic model, sulphate, acid neutralising capacity, critical loads, lake chemistry, soil base saturation.

Introduction

During the 1970s and 1980s, the acidification of surface waters by atmospherically deposited sulphur (S) became a major international concern. Major S emission control programmes were implemented in North America, resulting in current emissions being ~30% less than in 1980 (Jeffries *et al.*, 2000). As a result, sulphate (SO_4^{2-}) deposition in south-central Ontario has decreased by ~40% in the past two decades. Consequently, SO_4^{2-} concentrations in headwater lakes and their inflows have decreased (Jeffries *et al.*, 1995; McNicol *et al.*, 1998; Stoddard *et al.*, 1999). However, the level of acidic deposition remaining is still unlikely to promote widespread recovery of aquatic ecosystems (Jeffries *et al.*, 2000; Henriksen *et al.*, 2002; Aherne *et al.*, 2003a).

Steady-state (critical load) models have been applied recently in south-central Ontario to evaluate the adequacy of existing S emission control programmes in eastern North America. Critical loads of acidity were estimated for ~1500 lakes using the Steady-State Water Chemistry (SSWC) model (Henriksen *et al.*, 2002). In addition, critical loads of S and nitrogen (N) were estimated for a sub-set of these lakes (285) using the First-order Acidity Balance (FAB) model (Aherne *et al.*, 2003a). However, although steady-state models yield an estimate of the *ultimate* chemical state, they do not allow determination of when this state will be reached. Dynamic acidification models are required to estimate the time involved in attaining a certain lake chemical state in response to changes in deposition (Posch *et al.*, 2001).

Several dynamic process-oriented models have been developed to investigate the response of surface waters to acid deposition (Tiktak and van Grinsven, 1995). Three soil chemical models have been widely used for simulating acidification responses in soils and freshwaters: MAGIC (Cosby *et al.*, 1985), SAFE (Warfvinge *et al.*, 1993) and SMART (De Vries *et al.*, 1989). These models have been applied also on a regional scale: Europe (De Vries *et al.*, 1994), southern Norway (Cosby and Wright, 1998), southern

Sweden (Alveteg *et al.*, 1995), Switzerland (Kurz *et al.*, 1998) and the United Kingdom (Evans *et al.*, 1998). In recent years, there has been increasing recognition of the importance of dynamic models in developing emission reduction targets. Under the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (LRTAP), work is currently underway to apply dynamic models on a European scale to support future re-negotiations of the Gothenburg Protocol (UNECE, 2001).

This paper presents a regional application of the dynamic model MAGIC (model of acidification of groundwater in catchments) to 25 lakes in south-central Ontario. These lakes represent a sub-set of the regional data-set used in the previous steady-state investigations. The objectives of the research were to investigate the historic chemical variations through time in response to changing deposition, and to assess the impact of recently proposed S emission reductions on future lake water chemistry. The proposed S emission reduction scenario is based on Canada's post-2000 Acid Rain Strategy and the proposed Clear Skies Legislation in the United States (Kaminski, 2002).

Study area

The study lakes are located in the District of Muskoka and the counties of Haliburton and Nipissing in south-central Ontario (Fig. 1), a region that for decades has received substantial levels of acid deposition (Dillon *et al.*, 1987). The majority of the lakes are sensitive to the deposition of strong acids because of their geological setting on the southern extension of the Canadian Precambrian Shield (Neary and Dillon, 1988). Bedrock in the region is primarily granitised biotite and hornblende gneiss, with lesser areas of amphibolite and schist. The soils are poorly developed, typically podzols and brunisols formed on coarse-grained thin glacial till. The economy of the region is controlled largely by activities related to recreation and tourism, with cottage developments (seasonal and permanent) common throughout the region.

The land cover is dominated by semi-natural mixed hardwood forests; catchments are dominated by sugar maple (*Acer saccharum*) and red maple (*Acer rubrum*), with some American beech (*Fagus grandifolia.*), yellow birch (*Betula alleghaniensis*), red oak (*Quercus rubra*), eastern hemlock

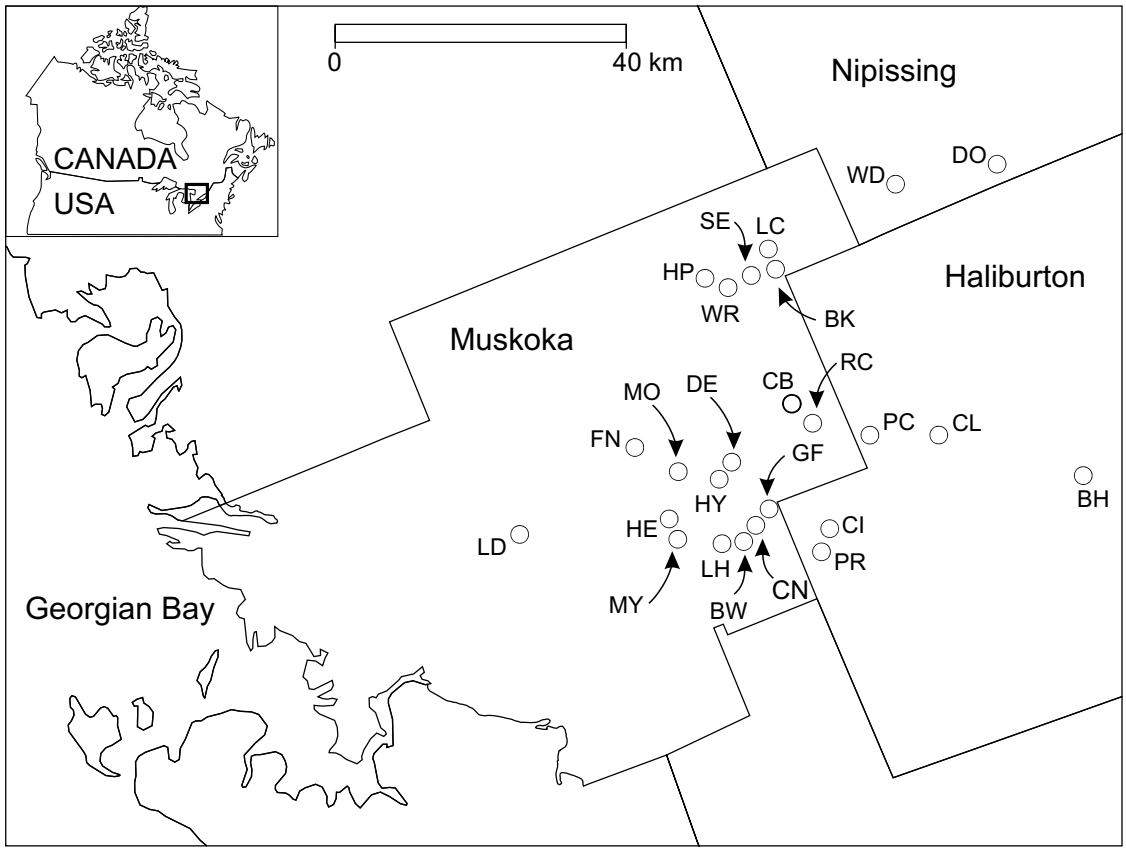

Fig. 1. *Location of the 25 study lakes in the district of Muskoka and the counties of Haliburton and Nipissing, south-central Ontario, Canada (see Table 1 for lake names).*

(*Tsuga canadensis*) and white pine (*Pinus strobus*). Small wetlands, dominated by white cedar (*Thuja occidentalis*) and black spruce (*Picea mariana*), are ubiquitous throughout the entire region, covering an estimated 10% of the total area. Nutrient cycling in the catchments of several of the study lakes (Plastic, Harp, Chub and Red Chalk) has been studied extensively (Watmough and Dillon, 2003a).

The climate of the study area is north temperate; long-term annual average precipitation is approximately 1000 mm, about one quarter to one third of which falls as snow. Approximately half of the precipitation produces stream runoff (Table 1). The mean monthly air temperatures for January and July are –10°C and 19°C, respectively, and the long-term annual average temperature is approximately 5°C.

Model description

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on soil and surface water chemistry. The model was first described by Cosby *et al.* (1985) and more recently by Cosby *et al.* (2001). In brief, the model predicts monthly and annual average concentrations of the major ions for soil solution and surface water chemistry. MAGIC represents the catchment with aggregated, uniform soil compartments (one or two) and a surface water compartment that can be either a lake or a stream. Time-series inputs to the model include annual or monthly estimates of: deposition of ions from the atmosphere (wet plus dry deposition), discharge volumes and flow routing within the catchment,

Table 1. Lake name, calibration year, lake area (relative to catchment area), water retention time, long-term mean annual runoff (Q) and selected chemistry for the 25 study lakes. Lake chemistry data are presented as a three-year annual average centred on the calibration year.

ID	*Lake name*	*Year*	*Area* %	*Retention* years	*Q* mm	*pH*	Ca^{2+}	Mg^{2+}	SO_4^{2-}	*DOC*
								$\mu mol_c\ L^{-1}$		$mg\ L^{-1}$
BH	Basshaunt	1994	5.6	1.0	429	6.66	201.6	84.2	135.3	4.1
BW	Bigwind	1993	21.9	5.0	464	6.27	119.2	46.0	134.8	3.2
BK	Buck	1994	13.8	2.7	561	6.44	140.9	61.0	123.9	2.9
CB	Chub	1997	11.2	2.0	490	5.70	93.7	44.9	117.2	4.8
CI	Cinder	1990	8.3	1.6	431	5.80	117.0	56.2	137.8	5.3
CL	Clear	1993	28.4	7.5	470	5.79	111.3	44.2	152.4	1.7
CN	Crosson	1997	9.8	1.6	558	5.64	84.7	39.4	109.8	4.1
DO	Delano	1992	9.7	1.4	489	5.96	138.6	73.7	164.7	5.7
DE	Dickie	1997	18.7	1.8	517	6.00	122.2	48.1	104.7	4.6
FN	Fawn	1991	5.7	0.4	514	5.72	135.1	55.0	134.2	9.1
GF	Gullfeather	1994	6.3	0.6	472	5.58	100.5	40.4	119.4	6.1
HP	Harp	1997	13.2	3.2	549	6.35	133.5	67.9	125.1	3.7
HE	Healey	1991	16.5	1.0	481	6.17	128.3	47.8	122.4	6.1
HY	Heney	1997	23.0	1.5	515	6.20	73.8	37.3	91.6	3.3
LH	Leech	1991	24.3	3.3	469	6.11	135.3	54.6	152.5	4.3
LD	Leonard	1991	28.3	3.8	519	6.03	115.8	47.6	140.1	3.0
LC	Little Clear	1994	1.9	0.3	565	6.48	158.8	73.5	132.6	2.4
MY	Mckay	1991	14.3	1.6	472	6.19	152.0	58.2	153.9	5.2
MO	Moot	1991	5.3	0.3	508	5.64	103.1	40.4	106.7	6.9
PC	Plastic	1997	25.2	4.0	502	5.77	75.1	31.6	112.0	1.9
PR	Poker	1991	7.0	1.1	423	6.06	123.7	72.6	129.7	5.7
RC	Red Chalk	1997	16.9	3.6	543	6.36	111.7	58.9	117.7	2.6
SE	Solitaire	1995	24.7	5.8	568	6.57	128.8	58.9	128.8	2.3
WR	Walker	1995	20.9	2.3	575	6.61	158.4	69.3	120.7	3.6
WD	Westward	1993	27.6	11.5	493	6.25	104.8	46.5	116.1	1.5
	Mean		15.5	2.7	503	6.09	122.7	54.3	127.3	4.2
	Median		14.3	1.8	502	6.11	122.2	54.6	125.1	4.1

biological production, removal and transformation of ions, internal sources and sinks of ions from weathering or precipitation reactions, and climate data. Constant parameters in the model include physical and chemical characteristics of the soils and surface waters, and thermodynamic constants. The model is calibrated using observed (or 'target') values of surface water and soil chemistry for a specified period. The eight site-measured target variables are: surface water concentrations and soil exchangeable fractions for base cations, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}). In this instance, calibration refers to an automated optimisation procedure that is a component of the MAGIC model suite (MAGICOPT) generally used for regional applications. Prior processing, or calibration, of the model data is described under 'regional modelling approach'.

In the current study, all catchments were represented using one soil compartment receiving deposition and releasing discharge to the lake compartment. The soil compartment represents the aggregated horizons of the catchment soils. Simulations were carried out using an annual time-step, with a number of simplifying assumptions applied consistently across the region. It was assumed that forests were at steady state and harvesting removals were negligible; as such, biological production and removal were ignored. Discharge volume and flow routing within the catchments were not varied through time; discharge was described using long-term means with 100% routed to the lake. Detailed process-oriented N dynamics were not modelled, rather, N retention was set to match observed lake concentrations. The essential data for the regional site-specific application are time-series of annual atmospheric deposition (wet plus dry), physical and chemical characteristics of the soils and lakes, and observed soil and lake chemistry for each study lake.

Data sources

LAKES

Chemical data for lakes (~1500) in south-central Ontario have been collected under different research projects and lake surveys since the late 1970s. The current study focuses on a sub-set of the regional data-set that includes only those lakes monitored for 10+ years (25 lakes: Fig. 1, Table 1). Annual chemical concentrations were derived from 1–8 whole-lake, morphometrically weighted samples collected during the ice-free period. During the 1980s, these lakes were sampled monthly; more recently, this has been reduced to one or two samples per year. The exception was a set of lakes, known as the 'A lakes' (Chub, Crosson, Dickie, Harp, Heney, Plastic and Red Chalk), that have been studied extensively for over 20 years (Dillon and Molot, 1997). For these lakes, data were collected throughout the year as whole-lake, morphometrically weighted samples (Dillon *et al.*, 1997). Depending on the year, between 8 and 26 samples were collected per lake. All chemical analyses were carried out at Ontario Ministry of the Environment laboratories, either at Dorset or Toronto (OME, 1983).

During the period 1980–1998, the number of years with available data for the 25 lakes in this study ranged from 10 (Cinder Lake) to 19 (A lakes). The most recent consecutive three-year period was used to describe observed annual average lake concentration data (targets) for model calibration (Table 1). As such, the calibration year (centred on the three-year period) ranged from 1991–1997. Lake area and bathymetry have been measured for all of the study lakes (Girard and Reid, 1990). The majority of the lakes are headwater lakes (17); as a result, catchment to lake area ratios are relatively high and water replenishment rates are long (median: ~2 years; Table 1). Catchment discharges were derived from a provincial runoff map generated from measured 30-year average runoff at all long-term hydrometric gauging stations throughout Ontario. The 30-year annual average runoff for all study lakes is ~500 mm yr^{-1} (Table 1).

SOILS

Soil data for south-central Ontario is limited to a few intensive studies. Soil bulk density, cation exchange capacity (CEC) and exchangeable base cation fractions have been measured recently (1999–2000) at seven sub-catchments (Watmough and Dillon, 2003a). The soils of two of these sub-catchments (Plastic and Harp Lakes) were sampled previously in 1983 (Lozano, 1987). In general, soil physical and chemical properties are uniform across the region; soil depth rather than chemistry is the most important factor in determining acid sensitivity in the study area. As such, all available soil data for the region were aggregated into one set of values, weighted by depth and bulk density, to produce default regional physical and chemical characteristics for the soils (Table 2). This set of default values was applied uniformly across the region.

DEPOSITION

Bulk deposition has been measured in Muskoka and Haliburton during the past two decades (Dillon *et al.*, 1988; Henriksen *et al.*, 2002). Either four (1980–1989) or three (1990–present) stations were used to generate annual deposition for the Muskoka-Haliburton region, which was

Table 2. Fixed input parameters and soil calibration targets for the regional application. Soil depth, soil SO_4^{2-} adsorption maximum capacity and lake DOC concentration are presented as ranges (minimum–maximum) as their values vary between the study lakes.

Parameter	*Units*	*Soil*	*Lake*
Depth †	m	0.31–1.30	—
Porosity	%	35	—
Bulk density	kg m^{-3}	900	—
Cation exchange capacity (CEC)	$mmol_c$ kg^{-1}	70	—
SO_4^{2-} adsorption half saturation	$mmol_c$ m^{-3}	2500	—
SO_4^{2-} adsorption maximum capacity †‡	$mmol_c$ kg^{-1}	0.1–1.1	—
Aluminium solubility constant	log	9.2	7.5
Temperature	°C	6.5	6.5
Partial pressure of CO_2	% atm	0.55	0.05
Dissolved organic carbon (DOC) †	mmol m^{-3}	55	2–48
Soil calibration targets:			
Exchangeable Ca^{2+} fraction	% of CEC	13.7	—
Exchangeable Mg^{2+} fraction	% of CEC	4.0	—
Exchangeable K^+ fraction	% of CEC	2.2	—
Exchangeable Na^+ fraction	% of CEC	2.1	—

† Range refers to values from individaul catchments. ‡ Range obtained through calibration.

assumed to be representative of deposition to the study area. The current annual average bulk depositions (1995–1999) for S and N are 41.1 $mmol_c$ m^{-2} yr^{-1} and 62.5 $mmol_c$ m^{-2} yr^{-1}, respectively (Aherne *et al.*, 2003a). Total deposition was estimated using dry deposition factors derived from throughfall measurements in the region (Neary and Gizyn, 1994).

Sulphate deposition history was reconstructed from historic S emission inventories (1850–1940: Husar, 1994; Lefohn *et al.*, 1999; 1940–1980: EPA, 2000) and observations (Fig. 2). Similarly, nitrate (NO_3^-) deposition history was reconstructed from emission inventories (1850–1940: Husar, 1994; 1940–1980: EPA, 2000) and

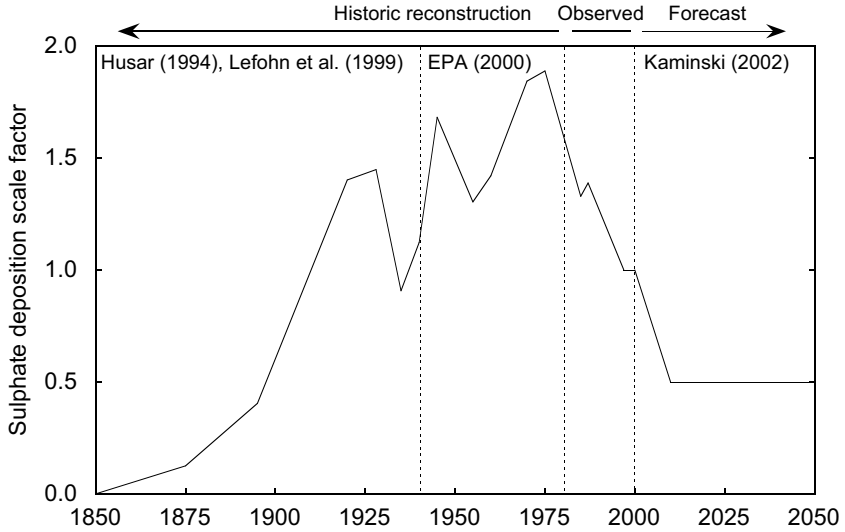

Fig. 2. *Estimated historic and future sulphate deposition (scale factor; 1997 deposition (41 μmol_c L^{-1}) is equivalent to a factor of 1.0) for the period 1850–2050. The broken lines separate the different data sources used to construct the deposition sequence.*

observations. North American emission inventories for ammonia (NH_3) are rather scarce. As such, a simplified ammonium (NH_4^+) deposition sequence was constructed from observations, and NO_3^- emission data in combination with global emission estimates of NH_3 (Galloway, 1995). Given the simplified treatment of N dynamics in the current study, model outputs will not be affected significantly.

Sulphate deposition forecasts were derived from recently proposed emission reduction estimates using the Acid Deposition and Oxidant Model (ADOM; Kaminski, 2002). The proposed reductions correspond roughly to a 50% reduction in SO_4^{2-} deposition by 2010 from 2000 baselines. Sulphate deposition was assumed constant thereafter. Deposition forecasts for NO_3^- and NH_4^+ were assumed to remain constant at current levels (annual average bulk depositions (1995–1999) for NO_3^- and NH_4^+ are 36.6 $mmol_c$ m^{-2} yr^{-1} and 25.9 $mmol_c$ m^{-2} yr^{-1}, respectively). In addition, deposition sequences for all other ions were assumed to be constant throughout the simulation period.

Regional modelling approach

The objective of the regional site-specific approach was to apply a uniform modelling methodology to all study lakes using regionally consistent data. Previous dynamic modelling assessments in the study area have been confined to single site applications (e.g., Seip *et al.*, 1985; Aherne *et al.*, 2003b). The regional application was carried out in three stages (Fig. 3).

Stage 1 involved the acquisition, collation and preparation of data. Site-specific parameter files were prepared using lake water and soil physico-chemical characteristics measured in the field (lake area, lake retention, soil bulk density, soil cation exchange capacity, etc.), and considered 'fixed' in the model (Tables 1 and 2). In addition, some default parameter values were applied uniformly across the region (Table 2), i.e. the partial pressure of carbon dioxide in the soil (pCO_2) was set at ~15 times atmospheric. Default values were based on laboratory (LaZerte and Findeis, 1994), field (LaZerte and Scott, 1996) and previous modelling studies in the region (Aherne *et al.*, 2003b). Chloride (Cl^-) and SO_4^{2-} were assumed to be in steady state with respect to input-output fluxes. The excess of outputs over inputs, which was attributed principally to unmeasured dry deposition, was resolved by adjusting individual dry deposition factors. The mean SO_4^{2-} dry deposition factor for the 25 study lakes was determined to be 1.17, which is similar to estimates from throughfall and dry deposition investigations in central Ontario (Sirois *et al.* 2001; Neary and Gizyn, 1994). The assumption that SO_4^{2-} is conservative is a simplification of the regional modelling approach. Numerous studies in North America and Europe have shown that SO_4^{2-} is not conservative (Dillon and LaZerte, 1992; Mitchell *et al.*, 2001; Prechtel *et al.*, 2001). If S adsorption has occurred historically, recovery times are likely to be greater than those predicted by the model. In general, SO_4^{2-} input-output imbalances were resolved using dry deposition factors; however, limit S adsorption was also implemented

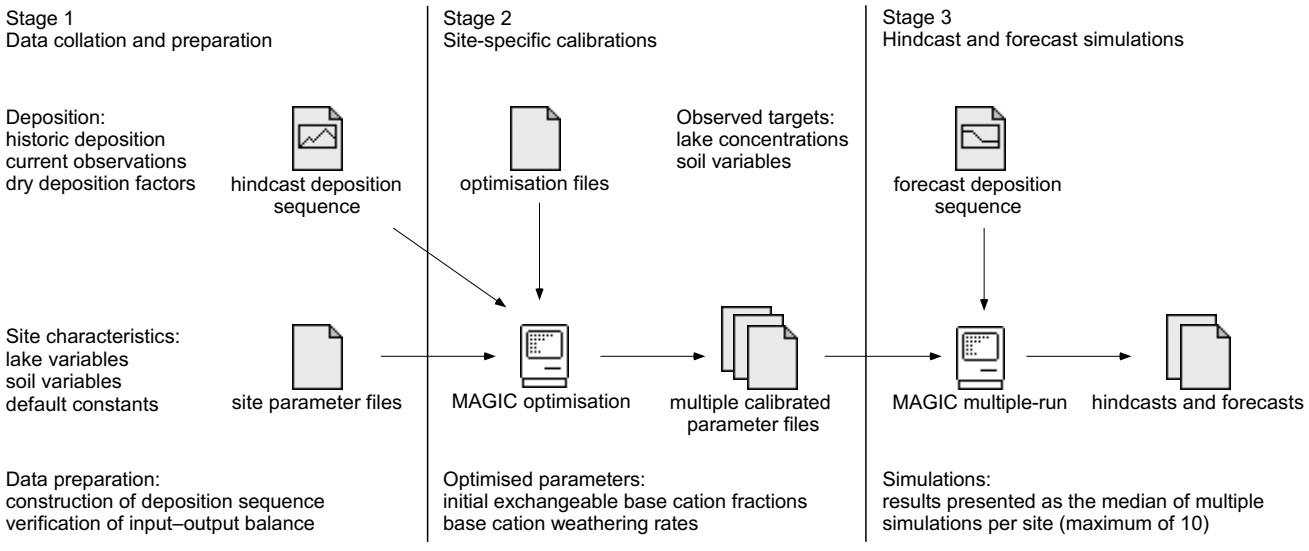

Fig. 3. *Stages in regional modelling approach: data collation and preparation, site-specific calibration, and hindcast and forecast simulations.*

to resolve any remaining slight imbalance (Table 2). Nitrogen (NO_3^- and NH_4^+) uptake and transformation was described as a catchment net retention calculated simply as the difference between input and output flux for the calibration year. This percentage was assumed to be constant throughout the simulation.

In Stage 2, base cation weathering rates and initial soil exchangeable fractions (and exchange constants) were calibrated to lake water and soil chemistry targets using an iterative automated optimisation procedure (MAGICOPT). The procedure uses numerical techniques to select parameter values that result in a minimum sum of squares error between simulated and observed target variables for each catchment. To account for uncertainty in a number of the fixed parameters (lake retention, lake area, soil depth, soil bulk density, cation exchange capacity and SO_4^{2-} adsorption half saturation), a 'fuzzy' optimisation method was employed. Multiple calibrations were carried out for each lake studied; during each simulation the fixed parameters were varied randomly within the uncertainty bands specified (± 10%). In addition, uncertainty bands (or tolerance levels) were also applied to the target lake water (± 2 $\mu mol_c\ L^{-1}$) and soil chemistry (± 0.2 %) variables. For each study lake 10 calibrations were performed; any simulation that reproduced all target variables was considered successful.

Finally, hindcast and forecast simulations were carried out for each lake using all successful calibrations. Multiple simulation results for each lake were combined using median statistics to predict regional lake water chemistry for the period 1850–2050. In addition to time-series plots, changes in water chemistry were evaluated by comparing the distribution (histograms and cumulative frequencies) of water chemistry variables at four distinct time periods: 1875, 1975, 1997 and 2016, which correspond roughly to pre-acidification, worst case, current and future lake chemistry, respectively. Similar methods of evaluation have been employed in other regional modelling studies in North America (Clair *et al.*, 2003) and Europe (Jenkins *et al.*, 2003).

Results and discussion

REGIONAL CALIBRATIONS

Multiple calibrations were performed on simulations run from 1850 to 1997 using historical deposition sequences. The number of successful calibrations per study lake ranged from 8–10, with most lakes having 10 successful calibrations (16 lakes). As expected, there is excellent agreement between simulated and observed acid neutralising capacity

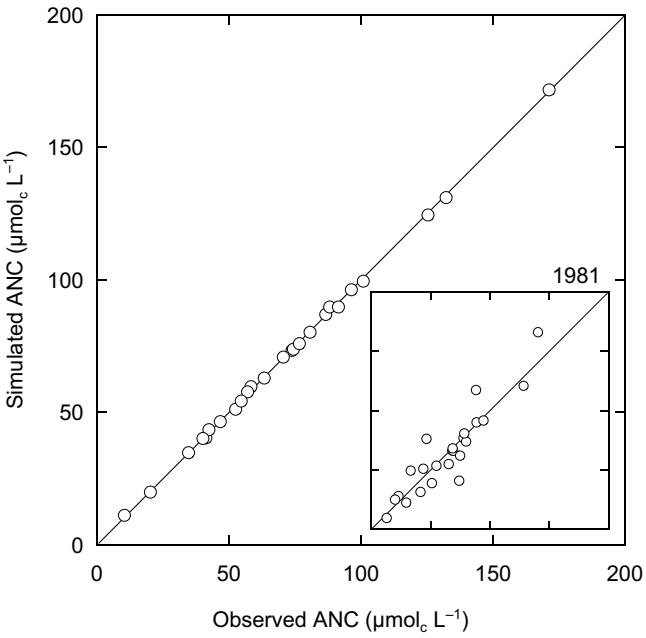

Fig. 4. *Observed and simulated acid neutralising capacity (ANC) during the calibration year (see Table 1) for the 25 study sites. The inset depicts observed and predicted ANC during 1981.*

(ANC: defined as the sum of base cations minus the sum of strong acid anions) for the calibration years (Fig. 4). For each of the lakes studied, more than 10 years of monitoring data are available. Simulated and observed ANC were also compared at the beginning of the monitoring period: 1981 (mean of three-year period centred on 1981). Goodness-of-fit was evaluated using linear regression of observed against predicted values (Janssen and Heuberger, 1995). In general, there is good agreement between simulated and observed ANC for 1981 ($R^2 = 0.85$; see inset, Fig. 4).

LAKE CHEMISTRY DISTRIBUTIONS

Once calibrated, soil and lake water chemistry for each lake was simulated for the period 1850–2050. The description of historical and future deposition drives the long-term reconstruction of surface water chemistry. As such, SO_4^{2-} deposition is the main driver. The historic deposition sequence reflects changes in energy consumption; the peak in emission in the 1970s (2 × current deposition) was followed by emission control programmes in North America (Fig. 2).

Changes in SO_4^{2-} deposition have a significant impact on lake chemistry, due to the assumption that SO_4^{2-} is conservative. Lake SO_4^{2-} concentrations follow the same trends as deposition with large changes in concentrations over time. However, spatially, there is very little variation

in concentration ranges between lakes (Fig. 5). In 1875, SO_4^{2-} was < 25 µmol$_c$ L^{-1} in all lakes, whereas by 1975 the majority of lakes had concentrations > 175 µmol$_c$ L^{-1}. In recent years, reduction in SO_4^{2-} deposition has resulted in recovery (modal value: 100–125 µmol$_c$ L^{-1}), which is predicted to improve further by 2016 (modal value: 50–75 µmol$_c$ L^{-1}). However, the proposed emission reductions will not return SO_4^{2-} concentrations to pre-acidification levels.

The sum of base cations (SBC) follows a similar pattern to SO_4^{2-}. However, spatially, there is a greater variation in values between lakes, reflecting the difference in catchment weathering rates (Fig. 5). In 1875, the modal value was estimated at 100–150 µmol$_c$ L^{-1}, which increased to 250–300 µmol$_c$ L^{-1} by 1975. This reflects the increased export of base cations from the soil exchangeable pool under high levels of acid deposition. The reduction in acid deposition by 1997 resulted in a modal value of 150–250 µmol$_c$ L^{-1}. By 2016, the SBC is predicted to recover almost completely to pre-acidification concentrations. This suggests that soil exchangeable pools in the region have become depleted of

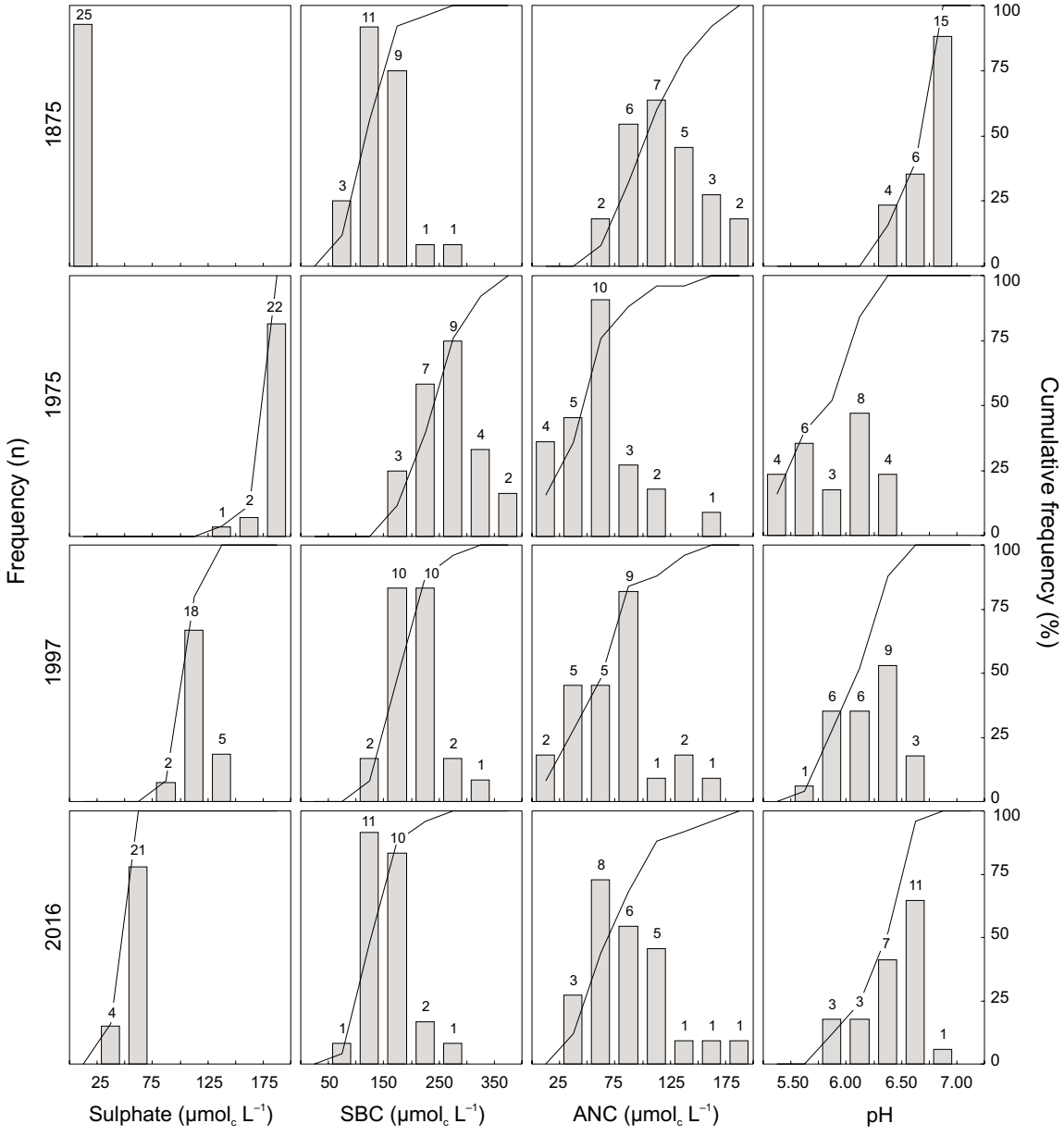

Fig. 5. *Distribution (histograms and cumulative frequencies) of sulphate, sum of base cations (SBC), acid neutralising capacity (ANC) and pH in the 25 study lakes during the years 1875, 1975, 1997 and 2016.*

base cations and have a reduced buffering capacity against acid deposition.

Modal ANC decreased from 100–125 $\mu mol_c\ L^{-1}$ in 1875, to 50–75 $\mu mol_c\ L^{-1}$ in 1975 and recovered partially to 75–100 $\mu mol_c\ L^{-1}$ in 1997. Although future predictions show the modal value at 50–75 $\mu mol_c\ L^{-1}$, there is a continued slight recovery as a greater percentage of lakes had ANC > 50 $\mu mol_c\ L^{-1}$ (88% as opposed to 72% in 1997). The absence of a significant recovery is due to the reduction in the SBC in 2016. The pH values show a pattern similar to that for ANC; historically high pH values shift to lower values during peak depositions and recover gradually under emission reductions. In 1875, the modal pH was 6.75–7.00. Under 1975 deposition, pH values show a bimodal distribution with one peak at 5.50–5.75 and another at 6.00–6.25. The lower values represent lakes that have limited buffering under the higher acid deposition load. By 1997, the bimodal distribution disappeared and there is gradual recovery (modal value: 6.25–6.50), with further recovery by 2016 (modal value: 6.50–6.75).

TIME-SERIES FOR pH AND ANC

Trends in lake acidification and recovery were evaluated using time-series for pH and ANC. The regional trends are presented as percentile time-series (Figs. 6 and 7).

In 1850, historic lake pH ranged from 6.30–7.00. Regional values for pH decreased smoothly until deposition started to change dramatically after 1900 (Fig. 6). Between 1950 and 1975, when acid load peaked, pH decreased by an average of 0.7 pH units, accompanied by a broadening of the range between percentiles, particularly for the lower percentiles. The lower percentiles reflect lake catchments that have a limited buffering capacity and low DOC

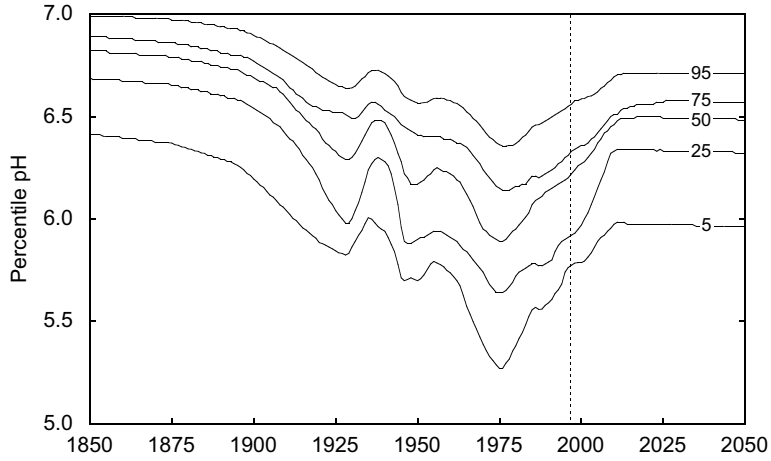

Fig. 6. *Simulated percentile time-series for pH during the period 1850–2050. The 5th, 25th, 50th, 75th and 95th percentiles are shown (small numbers in figure). The broken line separates hindcast and forecast simulations.*

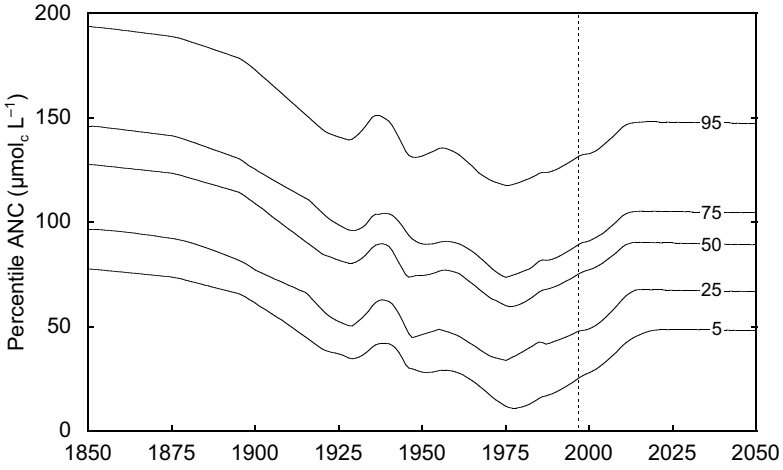

Fig. 7. *Simulated percentile time-series for acid neutralising capacity (ANC) during the period 1850–2050. The 5th, 25th, 50th, 75th and 95th percentiles are shown (small numbers in figure). The broken line separates hindcast and forecast simulations.*

concentrations. As a result, increases in acid deposition have a pronounced impact on pH in these lakes. During peak depositions, 50% of the lakes fell below pH 6.0. The decline in acid deposition from the late 1970s, and under the proposed future scenario, has a substantial effect on the pH. Significant recovery is predicted by 2050, with pentile (5th percentile) pH values estimated at 5.97.

ANC follows a similar pattern to pH (Fig. 7). However, unlike pH, which reacts rapidly to changes in deposition, acidification and recovery are noticeably buffered. All lakes had positive ANC throughout the entire simulation period and by 2050 the majority of the lakes had ANC > 50 $\mu mol_c L^{-1}$. A small number of lakes had high ANC values (95th percentile) reflecting catchments with higher weathering rates. A decrease in the range of ANC values in 2050 compared to 1850 reflects the depletion of base cations from the exchangeable pool. However, both ANC and pH show a recovery potential under the current deposition scenario and by 2050 concentrations levels have recovered to values predicted for the early 1900s.

In contrast, regional modelling studies for acid sensitive surface waters in Europe (Jenkins *et al.*, 2003) have reported widespread occurrence of ANC < 0 $\mu mol_c L^{-1}$ during the period of maximum SO_4^{2-} deposition (1980s). International agreements and European legislation to reduce S emissions have successfully promoted recovery across Europe (Evans *et al.*, 2001; Jenkins *et al.*, 2003). However, unlike south-central Ontario, model predictions for 2016 still indicate that a significant proportion of surface waters (in Norway, Sweden, Finland, Southern Alps and Southern Pennines, England) will have ANC < 20 $\mu mol_c L^{-1}$ (Jenkins *et al.*, 2003).

CRITICAL LOADS

Critical loads of acidity have been estimated recently for south-central Ontario using the SSWC (Henriksen *et al.*, 2002) and FAB (Aherne *et al.*, 2003a) models. The treatment of N dynamics in the current study is similar to the SSWC model; as such, the current discussion will be limited to the SSWC model. The SSWC pentile critical load of acidity for south-central Ontario was estimated at 33.7 $mmol_c m^{-2} yr^{-1}$ (Henriksen *et al.*, 2002), which is similar to the result of previous critical load studies in central Ontario (33.3 $mmol_c m^{-2} yr^{-1}$: Jeffries and Lam, 1993). The pentile critical load is typically used as a regional target to account for uncertainties, but also to ensure that a sufficient percentage of lakes is protected (95%). The SSWC critical load was based on an ANC limit of 40.0 $\mu mol_c L^{-1}$, which is the critical limit specified to protect aquatic organisms from damage. It is important to choose a value that is relevant to the specific lakes and their biota. Using the same chemical criterion and critical limit, a rough comparison can be made between SSWC critical loads and MAGIC predictions. In the current study, a regional pentile ANC of 40.9 $\mu mol_c L^{-1}$ was predicted by 2010; average total deposition in 2010 was 33.9 $mmol_c m^{-2} yr^{-1}$ (estimated from lake concentration and mean catchment runoff), which is in good agreement with the SSWC critical load.

SOIL EXCHANGEABLE FRACTIONS

Simulated future lake chemistry generally indicates a significant recovery compared to 1975 levels (Figs. 5–7). Similarly, future deposition is below the estimated critical load. However, simulations predict a continued decrease in soil exchangeable fractions of base cations and correspondingly base saturation. Simulations have been extended to 2100 to investigate the future long-term trends in base saturation (Fig. 8). The soil exchangeable base cations pools have been declining since the late 1800s, the period of greatest decline occurred during the 1900s, and although future simulations indicate a slower decline, recovery is not predicted.

Relative to 1850 there is a continued decrease in soil base saturation under the proposed emission reduction scenario (Table 3). A further 6% decrease in base saturation is predicted between 2016 and 2100. Exchangeable Ca^{2+} and Mg^{2+} follow the same trend; however, since the late 1900s there has been a shift from Mg^{2+} dominated losses to Ca^{2+} dominated losses (Table 3). Base cation losses from the exchangeable pool are currently buffering lakes against the impacts of acid deposition. This is only a temporary phenomenon and ultimately base cation inputs into lakes will decrease as exchangeable base cation pools become depleted. Indeed, simulations of lake water chemistry to 2100 predict that following the recovery between 1997 and 2016 (Figs. 5–7) there is further acidification between 2016 and 2100 (Table 3), with a 2.2% decline in ANC and 0.5% decline in pH values.

The recovery of soils by increases in base saturation will take much longer than recovery for lake chemistry. Soils that have been depleted by acid deposition will remain acid sensitive for a considerable period of time, as there will be little capacity to buffer acidity by cation exchange. The rate of recovery is dependent on base cation supply from weathering and atmospheric inputs. Regional simulations predict that although base cation losses have decreased in recent years, soils in the region will continue to acidify with Ca^{2+} losses dominating depletion of the exchangeable pool. The restoration of soil exchangeable base cation pools can only occur if weathering exceeds deposition plus natural

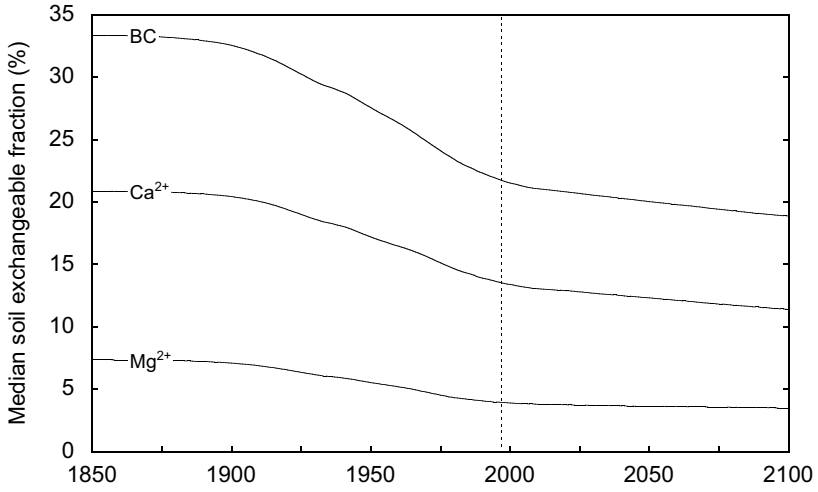

Fig. 8. *Simulated median soil exchangeable fractions for calcium (Ca^{2+}), magnesium (Mg^{2+}) and base cations (BC) during the period 1850–2100. The broken line separates hindcast and forecast simulations.*

Table 3. Simulated regional median lake concentration and soil chemistry for the 25 study lakes during the years: 1875, 1975, 1997, 2016 and 2100. Data are presented as percent decrease relative to simulated 1850 values.

Lake and soil variables (median of 25 study lakes)	*Percent decrease relative to 1850 (%)*				
	1875	*1975*	*1997*	*2016*	*2100*
Lake concentration					
Acid neutralising capacity †	3.2	52.8	40.9	29.2	31.4
pH	0.4	13.6	8.8	4.8	5.3
Soil chemistry					
Base saturation	0.4	27.7	34.9	37.3	43.3
Exchangeable Ca^{2+} fraction	0.3	27.5	35.2	37.9	45.3
Exchangeable Mg^{2+} fraction	0.6	38.3	46.3	48.6	52.3

† Acid neutralising capacity (ANC) = $(Ca^{2+} + Mg^{2+} + K^{+} + Na^{+} + NH_4^{+}) - (SO_4^{2-} - NO_3^{-} - Cl^{-})$

acidification. This clearly requires further emission reductions and will take many decades.

LIMITATIONS

The regional application is subject to a number of uncertainties and limitations, which can arise from two sources: input data and model structure. The largest data limitation relates to the spatial resolution of soil data; this can only be addressed by further soil sampling in the catchments of the study lakes. Uncertainty in model structure relates to processes not included or modelled, rather than model stability. In the current study, the impact of land-use, specifically the influence of forestry has been ignored. Tree harvesting is a common occurrence in south-central Ontario (Watmough and Dillon, 2003a); however, more research is needed to quantify adequately the removal of biomass through harvesting. Furthermore, the impacts of land use were beyond the scope of the current study. Inclusion of forest harvesting would result in slower recovery times than currently predicted by the model. Recent investigations in south-central Ontario, using the SSWC model, have shown that harvesting clearly has an enormous potential impact on lake chemistry, which will become more apparent as exchangeable base cation pools in soil decline and acid inputs can no longer be buffered (Watmough *et al.*, 2003b). Similarly, a number of other processes not included in the current study, e.g., concurrent declines in base cation concentrations, increasing NO_3^- concentrations, desorption of SO_4^{2-} from organic matter, and the oxidation of reduced

S compounds stored in wetlands, have all been shown to delay recovery.

Conclusions

The dynamic model MAGIC was applied to 25 lakes in south-central Ontario. The dynamic perspective of acidification complements previous steady-state modelling approaches used to evaluate the adequacy of existing emission controls in south-central Ontario. The objectives of the current study were to investigate the historic chemical variations in response to changing deposition and assess the impact of recently proposed S emission reductions on future lake water chemistry. Model simulations predict clear links between lake acidification and the deposition of strong acids. During the past two decades, decreased SO_4^{2-} deposition has resulted in significant recovery, which is predicated to improve further by 2050. Under the current deposition scenario, lake water concentrations in 2050 have recovered to levels predicted for the early 1900s, with the majority of the lakes having ANC > 50 $\mu mol_c L^{-1}$. In contrast, model predictions for Europe indicate that a significant proportion of acid sensitive surface waters (in Norway, Sweden, Finland, Southern Alps and Southern Pennines, England) will have ANC < 20 $\mu mol_c L^{-1}$.

Although regional simulations predict that base cation losses have decreased in recent years, soils in the region will continue to acidify with Ca^{2+} losses dominating depletion of the exchangeable pool. The restoration of soil exchangeable base cation pools can occur only if weathering exceeds deposition plus natural acidification. This clearly requires further emission reductions and will take many decades.

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